Cost Effective Laser Processing of Graphene Oxide, Transition Metal Oxides and Alginate Composite for Hybrid Electrodes for Supercapacitors

Pablo García Lebière*, Afroditi Koutsogianni, Joaquim Gispert, Miquel Minguillon, Angel Pérez del Pino, Enikö György
Instituto de Ciencia de Materiales de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain
*e-mail: pgarcia2@icmab.es

INTRODUCTION

Graphene-like materials

- Outstanding physical and chemical properties for energy storage → supercapacitors
  - → intrinsic electric conductance
  - → high specific surface area
  - → good flexibility
  - → fast charge-discharge rate
  - → cycling stability
  - → long lifetime

Reduced graphene oxide as EDLC

- Graphene oxide is reduced (rGO)
- Electrochemical double-layer capacitor (EDLC)
  - → energy physically stored through accumulation of charges in the active surface of electrodes

TMO as pseudocapacitors

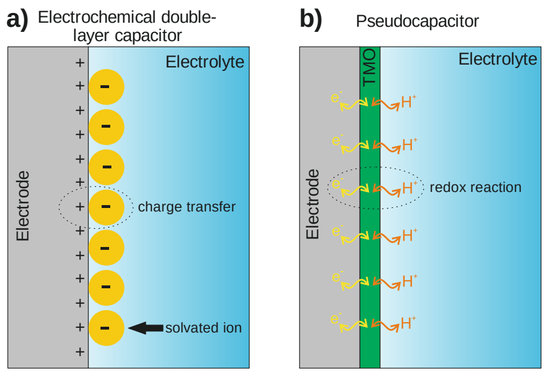
- Transition metal oxides (TMO) as pseudocapacitors
  - → Electrochemical energy storage carried out by fast and reversible redox reactions between electrode active material and electrolyte

Alginate to increase porosity

- Hydrogel formed by interaction of divalent ions from metal organic precursor

Laser processing

- Induce photothermal reduction of GO
- Crystallization of TMO nanostructures from metal organic precursors
- Calcination of the hydrogel
- Fast prototyping
- High throughput
- Environmental friendliness
- High precision



Schematic of the two different charge storage mechanism a) EDLC and b) pseudocapacitance

Hybrid electrodes

- Electrochemical capacitance enhances by combining pseudocapacitive and EDLC materials
- Adding porosity increases active surface

EXPERIMENTAL

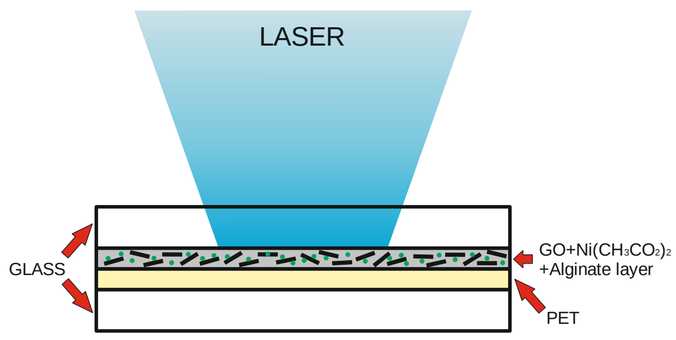
Layer preparation

1. Initial dispersions :
   a) GO 2.5 wt.%.
   b) GO 2.5 wt.%. + $Ni(CH_3CO_2)_2$ 1 wt.%.
   c) GO 2.5 wt.%. + $Ni(CH_3CO_2)_2$ 1 wt.%. + Alginic acid (alginate) 0.5 wt.%.
2. Stirring for 30 min, sonication during 2 min
3. 2.5 ml dispersion deposited over a PET substrate with a 1.5 x 5 cm^2 PDMS mask
4. Drying at room temperature for 48 hours

Irradiation conditions

- CW diode laser with wavelength of 450 nm
- Spot size Ø 400 µm
- Discretization of the irradiated area in pixels
  - → Each pixel is exposed to a certain irradiation time (t_{exp})
- No overlapping between pixels
- Layer irradiated compressed between two glass slides
  - → To avoid oxygen excess provoking layer burning

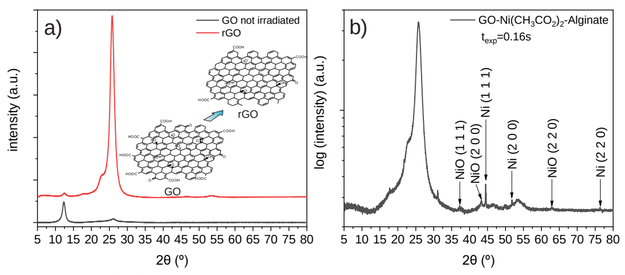
Initial dispersion of GO 2.5 wt.%. + $Ni(CH_3CO_2)_2$ 1 wt.%. + Alginate 0.5 wt.%. Both acetate and alginate are completely dissolved and GO is dispersed. No differentiation of compounds is observed



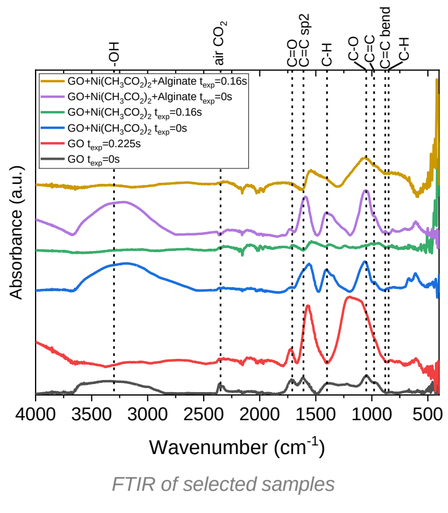
Scheme of laser irradiation of the deposited layers over a PET substrate, compressed between two glass slides

RESULTS AND DISCUSSION

Morphological and compositional studies

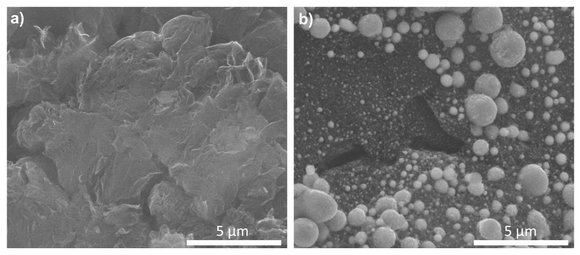


XRD θ/2θ patterns of a) GO after and before irradiation and b) GO-$Ni(CH_3CO_2)_2$-Alginate at t_{exp}=0.16s



FTIR of selected samples

- Initial GO is reduced to rGO
  → XRD peak shifts from ca. 12.5º to 26º
- rGO decorated with nanostructures
  → Metal organic precursor is decomposed
- The nanostructures are composed of Ni and NiO
- –OH group around 3500cm^{-1}, which belongs to carboxyl group –COOH, disappears after irradiation
  → Acetate decomposed enabling Ni-ions to form nanostructures
- C=O peak from de non-irradiated samples is reduced, increasing the C=C sp^2 peak



SEM images of a) GO layer irradiated with t_{exp}=0.22s and b) layer of GO-$Ni(CH_3CO_2)_2$ irradiated with t_{exp}=0.16s

Electrochemical studies

- Electrochemical cell → 0.5 cm^2 of electrode area
- Electrolyte → Na_2SO_4 1M
- Ag/AgCl as reference electrode

Cyclic voltammetry (CV)

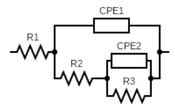
- Different exposure times for each initial dispersion
- Calculation of capacitance

$$C = {\int idV} \Big/ {2 \cdot \Delta V \cdot SR \cdot m}$$

- Rectangular-shaped voltammograms
  → capacitive nature
- Best specific capacitance of **90 F/g** for GO-$Ni(CH_3CO_2)_2$-Alginate

Impedance electrochemical spectroscopy (EIS)

- Small AC signal is applied around electrode E_{oc} and frequency sweep between 1 Hz to 200 kHz
- All electrodes fit with the same electric circuit



- R1 and R2 have low values
- R3 >5kΩ, low leakage
- CPE1 and CPE2 n value >0.7, near ideal capacitor

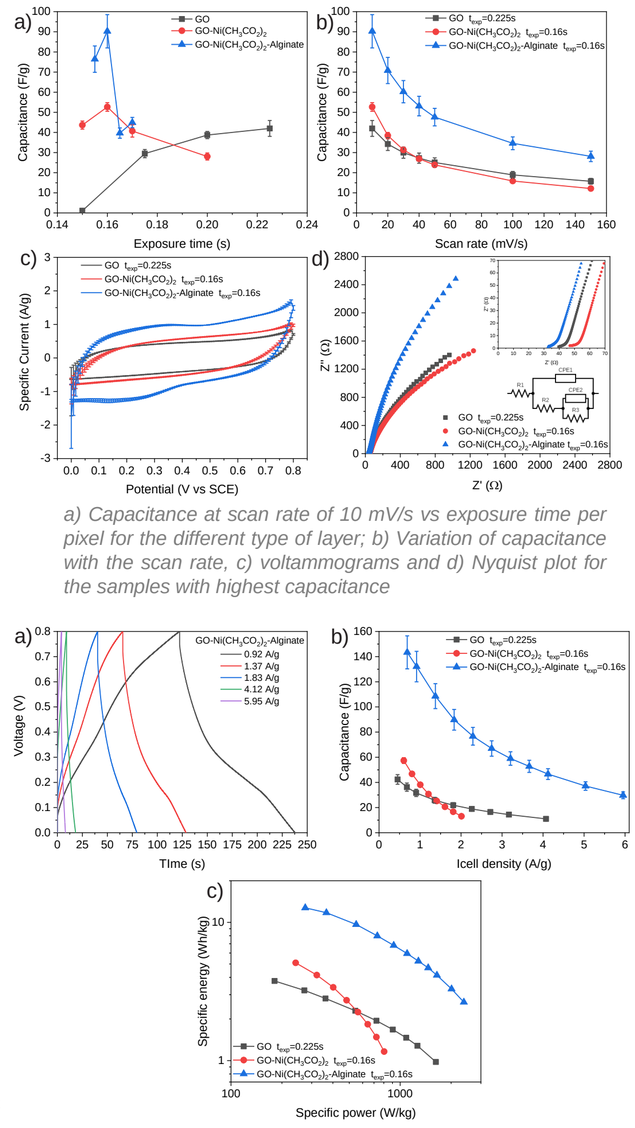
Galvanostatic charge-discharge (GCD)

- Triangular shape → capacitive behavior
- Calculation of capacitance

$$C = {I \cdot t_{disch}} \Big/ {\Delta V}$$

- Ragone plot: specific energy versus specific power

$$E = \frac{1}{2} CV^2 \qquad P = \frac{E}{t_{disch}}$$



a) Capacitance at scan rate of 10 mV/s vs exposure time per pixel for the different type of layer; b) Variation of capacitance with the scan rate, c) voltammograms and d) Nyquist plot for the samples with highest capacitance

a) GCD for different specific currents for electrode GO-$Ni(CH_3CO_2)_2$-Alginate; b) capacitance vs applied specific current and c) Ragone plot for the best samples

CONCLUSIONS

- The presented laser-based method can increase the specific capacitance ca. 30% over rGO by adding metal organic precursors (crystallization of TMO nanostructures), and ca. 65% over rGO-TMO layer by adding alginic acid (increase of porosity)
  → The obtained electrode combines EDLC and pseudocapactive mechanisms
- This laser-based method is easily-scalable
- Direct writing allows the design of specific patterns, for example IDEs
- Tuning the initial dispersion allows modification on the electrode performance
  → Great versatility, innovative laser-induced chemical reactions

ICMAB acknowledges the Severo Ochoa Program (MINECO, SEV- 2015-0496)

ACKNOWLEDGEMENTS
The authors acknowledge the financial support of the Spanish Ministry of Economy and Competitiveness under the project ENE2017-89210-C2-1-R.